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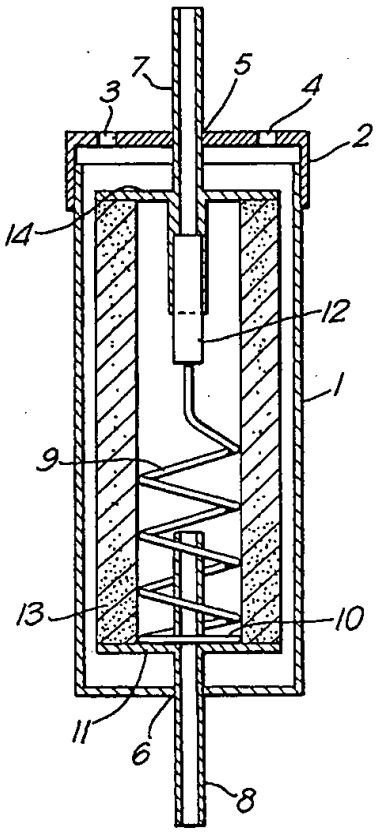
(54) Title: HYDROGEN GENERATOR

(57) Abstract

An autothermal reactor for producing high purity hydrogen from an organic feedstock, a source of oxygen and optionally water comprises a catalyst bed (13) for converting the feedstock into a hydrogen containing gas stream in association with a hydrogen diffusion membrane (9) which selectively separates hydrogen from the components of the gas stream. The hydrogen diffusion membrane preferably is in the form of a palladium based coil or spiral tube or a bundle of thin straight tubes or a palladium alloy supported on a porous ceramic substrate. The catalyst bed may be in the form of a granular bed of catalyst particles, a porous ceramic support material coated with catalyst, a porous ceramic foam coated with catalyst or a solid porous foam of catalyst. The catalyst bed and the hydrogen diffusion membrane preferably are located in the same reactor vessel and the catalyst bed is preferably positioned concentrically and coaxially around the hydrogen diffusion membrane.



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HYDROGEN GENERATOR

This invention relates to improvements in autothermal generators or reformers for the catalytic production of hydrogen from an organic fuel. More particularly, but not exclusively, this invention relates to improvements in self-igniting, self sustaining, autothermal catalytic hydrogen generators or reformers which can start up from ambient temperature.

The autothermal catalytic hydrogen generators or reformers to which this invention relates are of the type which can be operated by partial oxidation, steam reforming, water gas shift reaction or combinations thereof. Such reformers are disclosed in EP 0217532, EP 0262947 and WO 96/00186.

We have disclosed in EP 0217532, a self-igniting, self-sustaining, autothermal catalytic hydrogen generator or reformer the basic concept of which is that methanol and air are co-injected into the reactor containing an up-stream zone of a packed bed of a catalyst comprising copper on a refractory support with a down-stream zone containing a platinum or palladium catalyst mixed with a copper catalyst. The down-stream zone provides self-ignition to raise the reactor temperature to a point at which a hot spot is formed around the point of injection of feedstock into the upper bed of copper catalyst.

This hot spot concept was further developed in our invention disclosed in EP 0262947 which uses a reactor design which produces hydrogen from a hydrocarbon feedstock using a catalyst composed of platinum and chromium oxide on a support. Further details are given in a paper in Platinum Metals Review, 1989, 33 (3) 118-127.

In the course of scaling-up studies, we found, as described in WO 96/00186, that the output of the above mentioned reactors could be considerably increased by extending the injection/reaction zone interface whilst maintaining the short reaction time. This is achieved by replacing the single injector of the original hot spot reactors with a porous ceramic tube which acts as a multiple entry, high velocity, radial flow injection unit which causes a substantial pressure drop sufficient to prevent flow-back of feedstock or reaction products. The porous ceramic injection tube is surrounded by a shallow bed of catalyst so that the feedstock follows a radial path through the reactor. The catalyst is held in place by a copper gauze. A hot zone, as distinct from a hot spot, forms around the region where the feedstock enters the mass of the catalyst. It is believed that in the case of methanol feedstock, the hot

zone is preferably at a temperature of 350 to 600°C. It was found that copper-based catalysts were very effective for self-sustaining hydrogen generation but it was necessary, however, to add a small amount of a precious metal catalyst to provide self-ignition and also to raise the catalyst bed temperature to a level at which the catalytic reaction becomes self-sustaining. Water, preferably, is co-fed with the feedstock as the presence of water gives various beneficial effects, as described in WO 96/00186.

Through an iterative process of reactor engineering, catalyst design and performance mapping, we have dramatically improved the performance of the above type of reactors, especially for methanol processing. The reactor contains a single bed of multicomponent noble metals/base metal catalyst. It produces hydrogen as soon as methanol/air or methanol/air/water enters the reactor and it can reach steady state within a minute. The reactor converts methanol very efficiently by a combination of partial oxidation (exothermic), steam-reforming (endothermic) and water gas shift reaction. By supplying a feed of methanol/water/air, the exothermic and endothermic reactions can be made to sustain each other. Under these conditions, as much as 2.4 moles of hydrogen are produced for each mole of methanol consumed. Also, the maximum temperature inside the reactor is only 400°C excellent catalyst durability. As both the exothermic and endothermic reactions occur on the same catalyst particles, heat transfer occurs over very short (microscopic) distances as opposed to macro heat exchange.

The hot spot or hot zone types of autothermal reactor described above can be designed to operate with a variety of organic feedstocks and catalysts and also different forms of catalyst bed.

Whilst the present invention is described mainly with reference to the above type of hot spot or hot zone types of autothermal reactor it is to be understood that it can be applied also to more conventional designs of autothermal fuel processors.

The reformate gas mixture produced by reforming organic fuels in self-igniting, self-sustaining, autothermal catalytic hydrogen generators, as described above, typically contains hydrogen, methane, carbon monoxide, carbon dioxide, oxygen and nitrogen. The concentration of carbon monoxide in the reformate gas depends on several factors, including the composition of the feedstock, and can be as high as 10vol%. Such concentrations are too high for the reformate gas to be used directly in many industrial and laboratory

applications and steps have to be taken to lower the concentration of the carbon monoxide before use of the hydrogen-rich reformate.

The catalytic removal of carbon monoxide from a reformate gas mixture can be achieved by various techniques. These include (i) the selective oxidation of the carbon monoxide to carbon dioxide; (ii) the selective reduction of the carbon monoxide to methane; (iii) the reduction of the carbon monoxide with water vapour (water-gas shift) and (iv) the selective diffusion of hydrogen through a membrane which is more permeable to hydrogen than to carbon monoxide and other impurities of the reformate gas.

Several synthetic permeable membranes have been developed which can be used for selective separation and purification of hydrogen. These include noble metal membranes, ceramic membranes and zeolite membranes. One type of noble metal diffusion membrane comprises a thin palladium-based alloy tube (or tubes) in the form of a coil or spiral. Another type of noble metal membrane is in the form of a bundle of thin straight tubes. Yet another type of noble metal membrane consists of a thin layer of a palladium-based alloy supported on a porous ceramic substrate.

An objective of the present invention is to provide a self-igniting, self-sustaining, autothermal catalytic hydrogen generator which produces high purity hydrogen which can be used directly from the generator without further removal of carbon monoxide and other impurities.

According to the present invention there is provided an autothermal reactor for producing high purity hydrogen from an organic feedstock, a source of oxygen and optionally water comprising a catalyst bed for converting the feedstock into a hydrogen containing gas stream in association with a hydrogen diffusion membrane which selectively separates hydrogen from the other components of the gas stream.

Preferably, the catalyst bed and the hydrogen diffusion membrane are located in the same reactor vessel.

Further preferably, the hydrogen diffusion membrane is a palladium based membrane, a ceramic membrane or a zeolite membrane.

Suitably, the hydrogen diffusion membrane is a palladium based membrane in the form of a coil or spiral tube or in the form of a bundle of straight tubes.

Alternatively, the hydrogen diffusion membrane comprises a thin film of palladium alloy supported on the upstream hydrogen contacting surface of a porous ceramic substrate. A methanation catalyst may be deposited on the down stream surface of the porous ceramic substrate.

The catalyst bed may take the form of granular bed of catalyst particles; a porous ceramic support material coated with the catalyst; a porous ceramic foam coated with the catalyst or the catalyst bed may take the form of a solid porous foam of the catalyst itself.

Conveniently, the catalyst bed is positioned concentrically and co-axially around the hydrogen diffusion membrane.

In one embodiment of the invention the catalyst bed is in the form of a granular bed of catalyst particles and the palladium based coiled or spiral tube or bundle of straight tubes is buried in the granular bed of catalyst particles.

In another embodiment of the invention the coiled or spiral tube may be wrapped around the catalytic bed. In the reactor of the invention, the heat generated by the catalytic reaction is used to help sustain the operating temperature of the hydrogen diffusion membrane. In some systems, however, the operating temperature of the catalytic bed may be higher than the operating temperature of the hydrogen diffusion membrane so there may be a need to recover some heat from the reformate. Conversely, higher temperature diffusers may be applicable, actually operating at a similar temperature to the catalyst bed.

The reactor of the invention may operate by a combination of partial oxidation, steam reforming and water gas shift reaction.

Conveniently, the reactor of the invention is operated such that the temperature of the catalytic reaction is about the same or close to the optimum operating temperature of the hydrogen diffusion membrane.

The reactor of the invention suitably may form part of a fuel cell system or a gas chromatography system.

The reactor of the invention preferably operates on similar principles to the reactors disclosed in WO 96/00186 in that multi-point radial entry of feedstock into a catalyst bed causes a significant pressure drop and results in high velocity injection of the feedstock into the catalyst bed. However, in most embodiments of the reactor of the invention, the

feedstock enters from the outside of the catalyst bed and flows inwards through the bed, whereas the reverse arrangement is the case with the reactors described in WO 96/00186.

An embodiment of the invention will now be described, simply by way of example, with reference to the accompanying drawing which is a schematic cross-section of a reactor according to the invention.

Referring to the drawing, the reactor housing consists of a stainless steel cylinder 1, (height 12.5cm, diameter 5cm), closed at one end and with a stainless steel cover 2 fitted over the other end. The cover 2 is provided with inlet apertures 3 and 4 and an outlet aperture 5. The base of the cylinder 1 is provided with another outlet aperture 6. A flanged outlet tube 7 is fitted into outlet aperture 5 and another flanged outlet tube 8 is fitted into outlet aperture 6. A hydrogen diffusion membrane in the form of a palladium/silver alloy spiral tube 9 has one end 10 sitting on the flange 11 of outlet tube 8. The other end of spiral tube 9 is provided with a collar 12 which fits into the lower end of outlet tube 7. A solid permeable catalyst bed 13 is positioned concentrically and co-axially around spiral tube 9 and is retained between flange 11 of outlet tube 8 and flange 14 of outlet tube 7. The catalyst bed 13 may be located inside a porous ceramic multi-point feedstock injection tube (not shown) and may be held in position by a copper gauze (also not shown). Other designs of feedstock injection means may be utilised. A suitable catalyst bed composition is 5% Cu/Al_2O_3 and 5% Pd/Al_2O_3 mixed together in a ratio of 19:1 by mass.

A feedstock consisting of a liquid mixture of methanol and water mixed with air is vaporised outside the reactor and introduced into the reactor by means of inlet apertures 3 and 4. The feedstock passes from the outside of the catalyst bed 13 into the body of the catalyst where it is catalytically converted by a combination of partial oxidation, steam reforming and water gas shift reaction into a hydrogen-rich gas stream containing approximately 50% hydrogen. It is the combination of these reactions which makes the reactor autothermal. The hydrogen-rich gas stream leaves the catalyst bed 13 and passes across palladium/silver alloy spiral tube 9. The hydrogen diffuses through spiral tube 9 producing a gas comprising at least 99.995% hydrogen at 45psig pressure which leaves the reactor by means of outlet tube 7. The gaseous impurities in the hydrogen-rich gas stream which did not diffuse through spiral tube 9 leave the reactor as a bleed stream through outlet tube 8. The bleed stream can be catalytically burned to remove bleed hydrogen, trace

methanol and carbon monoxide. The heat from this after-burning can be used to heat the liquid entering the reactor or can be used somewhere else in the system.

The catalyst bed 13 operates at 8 to 10 bar pressure in order to generate enough pressure for the palladium/silver alloy spiral tube 9 to operate efficiently. This necessitates a compressor for the air and a liquid pump which can withstand these pressures. Furthermore, the hydrogen diffusion spiral tube 9 needs to operate at a minimum temperature of 300°C. The catalyst bed 13 may provide enough heat on its own to maintain the diffuser at its optimum operating temperature. The bleed stream of impurity gases which goes to vent through outlet tube 8 needs to be burned to remove any bleed hydrogen and methanol. The heat from this can be used to heat the feedstock liquids.

In another embodiment of the invention, the palladium/silver alloy diffusion tube 9 can be replaced by a bundle of straight palladium/silver alloy diffusion tubes.

In yet another embodiment of the invention, the palladium/silver alloy spiral diffusion tube 9 can be replaced by a hydrogen diffusion membrane in the form of a porous or microporous ceramic cylinder on the upstream surface of which is deposited a thin film of a palladium/silver alloy. The downstream surface of the porous cylinder may have deposited on it a methanation catalyst which would serve to mop up any carbon monoxide which penetrates through the hydrogen diffusion membrane due to pin hole leaks in the membrane. The catalyst bed and the ceramic-supported membrane are concentric and co-axial. The ceramic-supported palladium based membrane requires a much lower pressure differential across the membrane than a membrane in the form of a spiral tube or a bundle of straight tubes. A 3 bar pressure drop across the ceramic-supported membrane is typical, (and other types of hydrogen diffusion membranes may require even lower pressures). Furthermore, the heat generated by the catalytic reaction maintains the membrane at its preferred temperature of operation.

In yet a further embodiment of the invention, a hydrogen diffusion membrane in the form of a coil or spiral tube or in the form of a bundle of thin tubes may be buried in a catalyst in the form of a granular catalytic bed.

Also, the coil or spiral tube or bundle of straight tubes can be positioned around the outside of the catalyst bed with in this case the gas flow being from inside to the outside of the bed.

The autothermal reactor of the invention is particularly suitable for supply of pure hydrogen for small scale operations such as fuel cell systems for automotive purposes and for gas chromatography and other laboratory applications which require pure hydrogen. The present invention is particularly suitable for "portable" applications and does away with the need for hydrogen cylinders.

CLAIMS

1. An autothermal reactor for producing high purity hydrogen from an organic feedstock, a source of oxygen and optionally water comprising a catalyst bed for converting the feedstock into a hydrogen containing gas stream in association with a hydrogen diffusion membrane which selectively separates hydrogen from the other components of the gas stream.

2. A reactor according to claim 1 wherein the catalyst bed and the hydrogen diffusion membrane are located in the same reactor vessel.

3. A reactor according to claim 1 or claim 2 wherein the hydrogen diffusion membrane is a palladium-based membrane, a ceramic membrane or a zeolite membrane.

4. A reactor according to claim 3 wherein the hydrogen diffusion membrane is a palladium based membrane in the form of a coiled or spiral tube.

5. A reactor according to claim 3 wherein the hydrogen diffusion membrane is a palladium-based membrane in the form of a bundle of straight tubes.

6. A reactor according to claim 3 wherein the hydrogen diffusion membrane comprises a thin film of palladium alloy supported on the upstream hydrogen contacting surface of a porous ceramic substrate.

7. A reactor according to claim 6 wherein a methanation catalyst is deposited on the down stream surface of the porous ceramic surface.

8. A reactor according to any one of the preceding claims wherein the catalyst bed comprises a granular bed of catalyst particles.

9. A reactor according to any one of the claims 1 to 7 wherein the catalyst bed comprises a porous ceramic support material coated with the catalyst.

10. A reactor according to any one of claims 1 to 7 wherein the catalyst bed comprises a porous ceramic foam coated with the catalyst.

11. A reactor according to any one of claims 1 to 7 wherein the catalyst bed is in the form of a solid porous foam of the catalyst.

12. A reactor according to any one of the preceding claims wherein the catalyst bed is positioned concentrically and co-axially around the hydrogen diffusion membrane.

13. A reactor according to claim 4 or claim 5 wherein the catalyst bed is in the form of a granular bed of catalyst particles and the palladium based coiled or spiral tube or bundle of straight tubes is buried in the granular bed of catalyst particles.

14. A reactor according to claim 4 wherein the coiled or spiral tube is wrapped around the catalyst bed.

15. A reactor according to any one of the preceding claims wherein the heat generated by the catalytic reaction is used to sustain the operating temperature of the hydrogen diffusion membrane.

16. A reactor according to any one of the preceding claims which operates by a combination of partial oxidation and steam reforming.

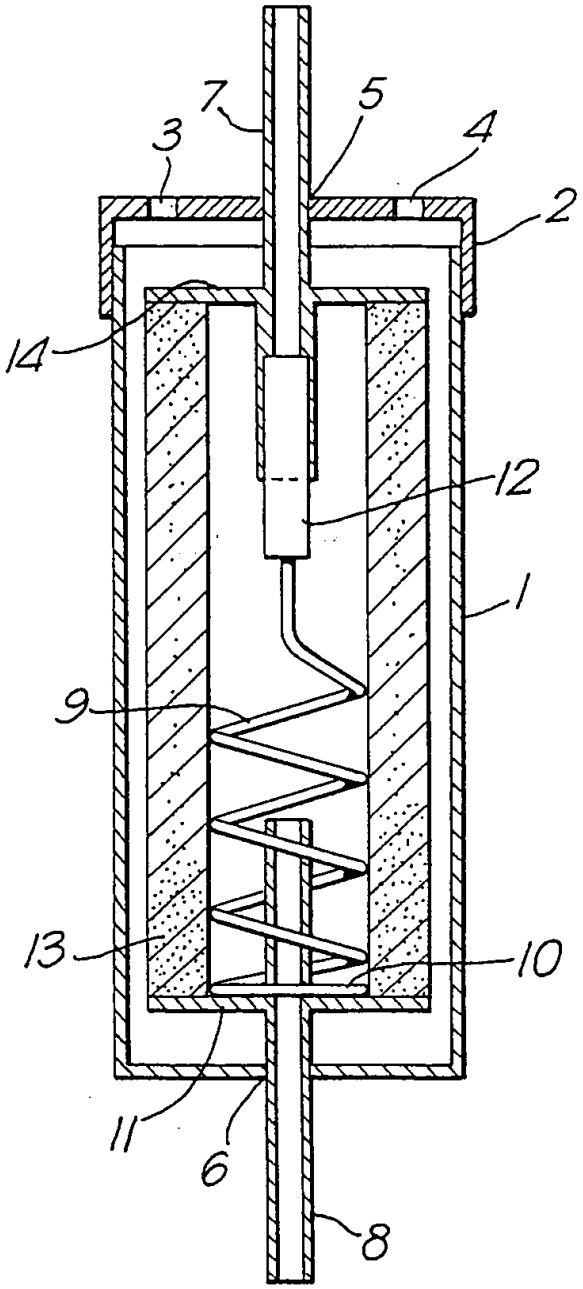
17. A reactor according to any one of the preceding claims which operates by a combination of partial oxidation, steam reforming and water gas shift reaction.

18. A reactor according to any one of the preceding claims in which the temperature of the catalytic reaction is about the same or close to the optimum operating temperature of the hydrogen diffusion membrane.

19. A fuel cell system comprising an autothermal hydrogen generation reactor as claimed in any one of claims 1 to 18.

20. A gas chromatography system comprising an autothermal hydrogen generation reactor as claimed in any one of the claims 1 to 18.

Fig.1.



INTERNATIONAL SEARCH REPORT

Int. .onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/38 C01B3/50 C01B3/48 H01M8/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 44 23 587 A (DAIMLER BENZ AG) 11 January 1996 see the whole document ---	1-3,5,6, 8,9,12, 13,15-19
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 004, 30 April 1996 & JP 07 315801 A (NGK INSULATORS LTD), 5 December 1995 see abstract	1-3,8, 16,19
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 455 (C-0987), 22 September 1992 & JP 04 160003 A (KAWASAKI HEAVY IND LTD), 3 June 1992 see abstract	1-3,5, 16,19
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Information on patent family members

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